# Eugen Sänger et al.– Ionization, Luminescence and the Chemical Ignition of Thermal Nuclear Reactions

A summary of two key papers.

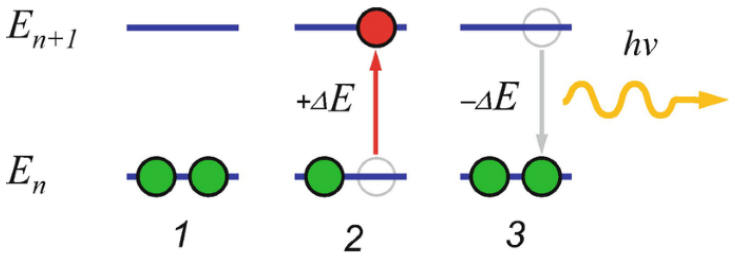
Eugen Sänger
(22 September 1905 – 10 February 1964)

sucked into a SCHRÖDINGER eigenstate vortex with its chaotic quantum mechanical phase space tentacles

# Part I.
# On the Ionization and Luminescence in Flames

# On the Ionization and Luminescence in Flames

By E. Sänger, P. Goereke and I. Bredt.

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**Abstract**

Reflection measurements using electrical waves on rocket gases show that the degree of ionization in flames must be significantly higher than previously assumed based on classical measurement and calculation methods. One explanation for this phenomenon may be that classical methods assume established equilibrium states, which cannot yet exist in flames, at least in the vicinity of the primary reaction zone. An approach to calculating the degree of ionization that takes into account equilibrium states that have not yet been established provides an explanation for the high ionization values measured. Calculating the energy content of the chemiluminescence radiation associated with ionization using the same principle allows us to interpret the processes involved in mixture preparation prior to the chemical reaction, for which a plausible physical explanation has not been possible until now.

# 1. Definition of Problem

When measuring the reflectivity and absorptivity of rocket exhaust jets for electrical waves, [15], values are obtained that can only be explained by a fire gas ionization that is ten times higher than that obtained by a standard calculation method for thermal ionization according to the Saha equation, [26], which reads as

$$\frac{N_h + N_\mathrm{e}}{N_h} = \frac{2}{\lambda_\mathrm{th}^3} \cdot \frac{f_\mathrm{ion} + f_\mathrm{el}}{f_\mathrm{ion}} \cdot e^{-\frac{W_0}{k_\mathrm{B} T}} .$$

(For explanation of symbols see section 3 and `https://en.wikipedia.org/wiki/Saha_ionization_equation`). In large rockets, 30 k to 350 kilograms of liquid fuel are prepared for combustion every second. The amount of heat required for the evaporation and heating of such quantities of fuel to ignition alone is in the order of $83\,\mathrm{kJ\,s^{-1}}$ to $420\,\mathrm{kJ\,s^{-1}}$. Convection and thermal gas radiation can only account for a few thousandths of this energy transfer, [30, 31]. *Chemiluminescence* (reaction glow)[1] is suspected to be the source of the apparent extraordinary additional heat sources.

In the following, after a brief reference to the determination of the degree of ionization from reflection measurements and its calculation according to the equation of Saha, an explanation will be sought for the strongly deviating results of measurements and calculations, taking into account the non-equilibrium states in the reacting fire gas. The calculation scheme developed is then able to explain the observed degrees of ionization and at the same time provides a means of calculating the preliminary stages of this ionization, namely chemiluminescence.

[1] See for an introduction `https://en.wikipedia.org/wiki/Chemiluminescence`.

The intensities of the reaction glow calculated in this way, on the other hand, make the processing operations in continuous furnaces understandable. The clarification of this indicated problem goes far beyond the field of rockets in terms of its technical significance and extends not only to all reaction engines and combustion engines, but also to general technical combustion, the problems of powder combustion, explosion and detonation processes, gas kinetics at very high altitudes and flight speeds, the technical application of atomic energy, etc.

# 2. On the Degree of Ionization of Flames through Reflection Measurements

The classic experimental methods for determining the ionization radius of a flame by measuring the conductive resistance between relatively cool electrodes have some major disadvantages. The finite thickness of the aerodynamic and thermal boundary layers on the electrode surfaces, with their low temperatures and adhering static boundary layers, lead to a shift in the ionization equilibrium and consequently act as electrically insulating layers, completely distorting the picture of gas conductivity and thus ionization.

Probe measurement methods are therefore less suitable for investigating the validity of the SAHA equation in flames. More suitable is the method of ionization measurement by reflection or absorption of electrical waves, which remains largely unaffected by the disturbance of the fire gas state by the measuring device. A series of experiments has established that flames can reflect very short electrical waves in the centimeter and, under certain circumstances, even in the millimeter wavelength range with a reflection coefficient approaching that of a metallic reflection. Due to the ease with which such short waves can be focused, it is possible and obvious to determine the highest degree of ionization of a flame in a manner analogous to ionosphere measurements. The state-of-gas conditions, which differ from those in the ionosphere, make it advisable to summarize the relationships underlying the measurement procedure for flames.

According to dispersion theory, the generally complex refractive index $n$ of a medium with a magnetic permeability of approximately 1 is a function of this frequency for an electric wave with a angular frequency $\omega = 2\pi \cdot f$. The influence of the Earth's magnetic field can be neglected at the high frequencies considered for measurements on flames. In addition, these frequencies are often so far outside the natural frequency ranges of the molecules of the fire gases that the influence of these natural frequencies should also be disregarded here. If we neglect the field-based influences of neighboring molecules polarized by the electric waves on the free electrons or ions, i.e., if the so-called SELLMEIER theory applies, [28], the refractive index $n$ follows

the relationship[2]:

$$n^2 - 1 = 4\pi \cdot \sum_{h=1}^{\infty} \frac{N_h \cdot \frac{e_h^2}{m_h}}{-\omega^2 + \mathsf{i}\,\omega\nu_h}\,. \tag{1}$$

Here, $e_h$ is the charge, $m_h$ is the mass, $\nu_h$ is the average collision number in the time unit with neutral molecules or atoms of an oscillator of type $h$. $N_h$ is the spatial density of the corresponding oscillator type, $\mathsf{i} = \sqrt{-1}$ is the imaginary unit vector.

Taking into account the influences of neighboring polarized molecules according to the theory of Lorentz-Lorenz leads to an expression that is proportional to $\frac{n^2-1}{n^2+1}$. Regarding the validity criteria of one theory or the other, please refer to the literature in [6]. Using the Lorentz theory, the measured values yield slightly higher ionization degrees (approximately 50 %) than using the Sellmeier equation. However, these deviations are small compared to the differences between the results of the reflection measurements and the calculation using the Saha equation, which often amount to several orders of magnitude. The minimum value provided by the Sellmeier equation should be used as the measured degree of ionization for the following considerations.

In thermal ionization through combustion processes (not nuclear reactions!), the probability of multiple ionization is very low. Near the reaction zone of a flame, i.e., at the location of the highest degree of ionization, the densities of free electrons and positive ions are therefore approximately equal. Since the influence of an oscillator on the refractive index $n$ is inversely proportional to the oscillator mass, the refractive index of this zone is determined practically only by the density of its free electrons. Therefore, the simplified relationship

$$n^2 = 1 + 4\pi \cdot \frac{N' \cdot \frac{e^2}{m}}{-\omega^2 + \mathsf{i}\,\omega\nu} \tag{2}$$

with the corresponding values for electrons applies to Equation 1.

Due to their higher diffusion velocity and the recombination of electrons, which occurs primarily through attachment to neutral molecules with the formation of negative ions, the electron density decreases much faster than the ion density with increasing distance from the reaction zone. The refractive index is then determined by the sum of the individual oscillator components according to Equation 1. Let the quantity

$$\sqrt{\frac{4\pi N' e^2}{m}} = \omega_0 \tag{3}$$

be designated as the "characteristic frequency" of the medium. If this has been determined by measurements, the electron density in the zone of strongest

[2]For an overview see `https://en.wikipedia.org/wiki/Sellmeier_equation`

ionization according to

$$N'_{(\mathrm{cm}^{-3})} = 3.15 \times 10^{-10} \cdot \omega^2_{0\,(\mathrm{s}^{-2})} \tag{4}$$

and the corresponding degree of ionization $\alpha_i$ at the same electron and ion density according to

$$\alpha_i = \frac{2N' \cdot k_\mathrm{B} T}{p} = 2.82 \times 10^{-22} \cdot N'_{(\mathrm{cm}^{-2})} \cdot \frac{T_{(^\circ\,\mathrm{K})}}{p_{\mathrm{kg\,cm}^{-2}}} \tag{5}$$

can be calculated by inserting the corresponding numerical values into Equation 3. In Equation 5, $k_\mathrm{B}$ denotes the Boltzmann constant, $T$ denotes the absolute temperature, and $p$ denotes the pressure of the gas.

In the ionosphere, due to the low gas density prevailing there, the influence of collision damping or the average collision rate $\nu$ per second of an oscillator with the neutral molecules or atoms of the medium on the refractive index can almost always be neglected. In flames, this neglect is not normally permissible without further ado, so that the influence of the collision rate on the reflection properties should be examined in more detail here.

With the phase factor $\mu$ and the damping factor $\varkappa$, the relationship

$$n^2 = (\mu + \mathrm{i}\,\varkappa)^2 = \varepsilon \tag{6}$$

exists between the complex refractive index $n$ and the complex dielectric constant $\varepsilon$ (absolute value $|\varepsilon|$) according to the definition described above. If we introduce the abbreviations

$$A \equiv 1 - \frac{\omega_0^2}{(\omega^2 + \nu^2)}\,,$$
$$B \equiv \frac{\nu}{\omega} \cdot \frac{\omega_0^2}{(\omega^2 + \nu^2)}$$

the Sellmeier equation can be written in the form:

$$\left|n^2\right| = |\varepsilon| = \sqrt{A^2 + B^2}\,, \tag{7a}$$

$$\mu = \sqrt{\frac{1}{2} \cdot \{|\varepsilon| + A\}}\,, \tag{7b}$$

$$\varkappa = \sqrt{\frac{1}{2} \cdot \{|\varepsilon| - A\}}\,. \tag{7c}$$

The equation for a plane wave propagating along the path $s$ in the medium after time $t$ is thus

$$\mathfrak{E} = \mathfrak{E}_0 \cdot e^{-\frac{\omega}{c} \cdot \varkappa \cdot s} \cdot e^{\mathrm{i}\,\omega \cdot \left(t - \frac{\mu}{c} \cdot s\right)}\,. \tag{8}$$

$\mathfrak{E}_0$ is the initial value of the electric field strength vector and $c$ is the propagation speed of the electric wave.

For simplicity, reflection measurements on flames will best be performed using electric waves incident approximately perpendicular to the flame axis. For the reflection factor $R$, i.e., the ratio of the reflected to the incident energy of a wave striking a homogeneous ionized gas layer from air ($n \approx 1$), we obtain

$$R = \left(\frac{\mathfrak{E}}{\mathfrak{E}_0}\right)^2 = \frac{(\mu-1)^2 + \varkappa^2}{(\mu+1)^2 + \varkappa^2}\,. \tag{9}$$

in this case. In Figure 1, the reflection factors calculated according to Equation 9 are shown as a function of the relative frequency $\omega_0/\omega$ or $f_0/f$ with the relative collision number $\nu/\omega_0$ as a parameter.

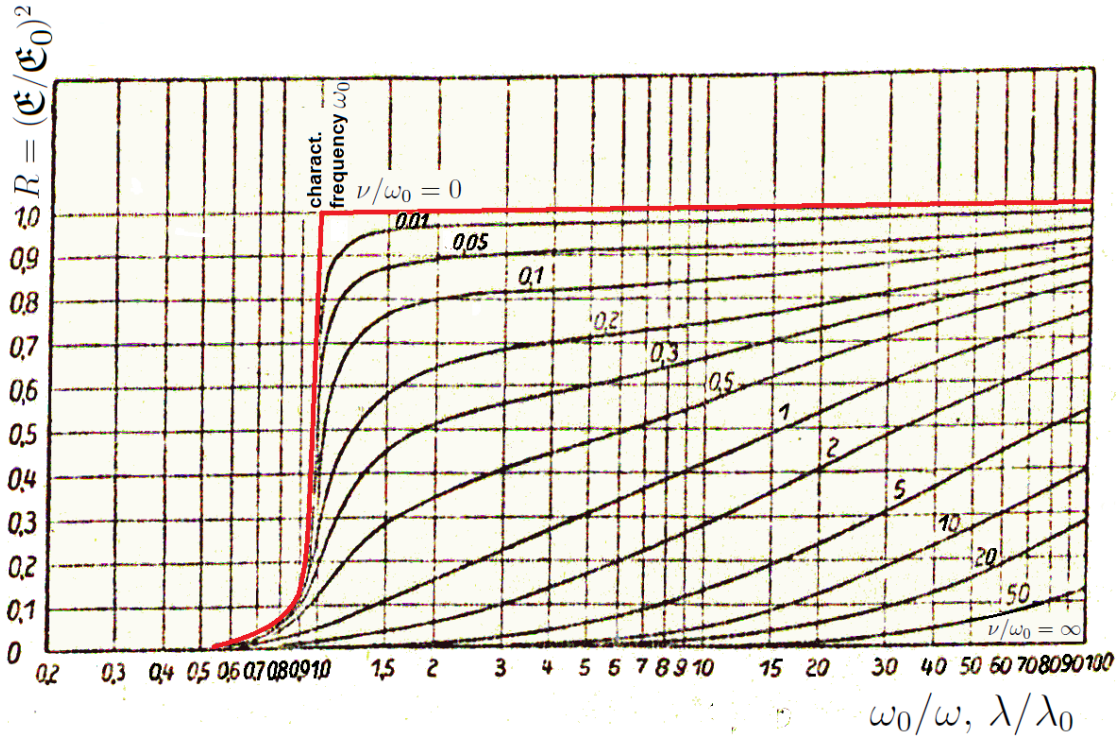



Figure 1: Reflectivity $R$ of a homogeneous, ionized gas layer over the relative frequencies $\omega_0/\omega$ or wavelengths $\lambda/\lambda_0$ with the relative collision number $\nu/\omega_0$ as a parameter

As can be seen from Figure 1, the transition from the reflective to the transmissivity state only occurs abruptly at the characteristic angular frequency $\omega_0$ if, as in the ionosphere, the influence of collision damping is insignificant. In this case, $\omega_0$ is identical to the so-called cut-off frequency. The greater the influence of collision damping, the smoother the transition from one state to the other and the less accurate the determination of $\omega_0$ from a measured reflection curve $R = g(\omega)$.

In reality, of course, a flame is not a homogeneous ionized medium; rather, as a result of diffusion and recombination, the degree of ionization decreases

both in the direction of the flame axis and radially away from it. Waves striking the flame therefore penetrate more or less deeply into the flame, depending on their frequency, until they encounter the degree of ionization required for their reflection. In doing so, they are attenuated according to Equation 8.

Deriving the relationships for calculating this case, in which electron and ion densities and collision rates are nonlinearly dependent on path length as a result of temperature changes, mixing of the combustion gases with the surrounding air, and diffusion phenomena, would go beyond the scope of this work. Some basic information on performing the calculation when the local distribution of the degree of ionization and collision rates is known can be found in [14, 10, 25, 11, 7, 8]. Here, only the result of such a calculation for waves that strike a flame coming out of the exhaust nozzle of a rocket at supersonic speed at a specific point is shown in Figure 2.

The characteristic course of these calculated curves corresponds well with measured reflection curves, especially in the vicinity of the characteristic frequency $\omega_0/\omega = 1$. For longer waves, however, the measured reflectivity decreased again, deviating from Figure 2. This is due to diffraction phenomena that become noticeable when the measured wavelength reaches the order of magnitude of the flame dimensions.

In most combustion processes, the Maxwell-textscBoltzmann velocity distribution largely applies to free electrons, and degeneration of the electron gas toward Fermi statistics can be expected at most in metal combustion. When Maxwell's velocity distribution applies, the expression

$$\nu = \sqrt{\frac{8\pi}{k_\mathrm{B} T \mu}} \cdot \sum_{i=1}^{n} r_i^2 \cdot p_i \tag{10}$$

can be derived for the average number of collisions per second ("Collision frequency") of an electron with neutral molecules, where $k_\mathrm{B}$ is Boltzmann's constant, $T$ is the absolute temperature, $r_i$ is the effective radius of a molecule of gas component $i$, $p_i$ is its partial pressure and $\mu$ is the reduced mass according to

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \,.$$

If only electrons are considered, the above formula is written in the form

$$\mu = \frac{m_\mathrm{el}^2}{2 \cdot m_\mathrm{el}} \,.$$

When deriving Equation 10, it was assumed that the average velocity of an electron due to the influence of the electric wave is small compared to the average thermal velocity. It is advisable to work with correspondingly low field strengths during the reflection measurements, as otherwise the collision frequency becomes non-linearly dependent on the effective value

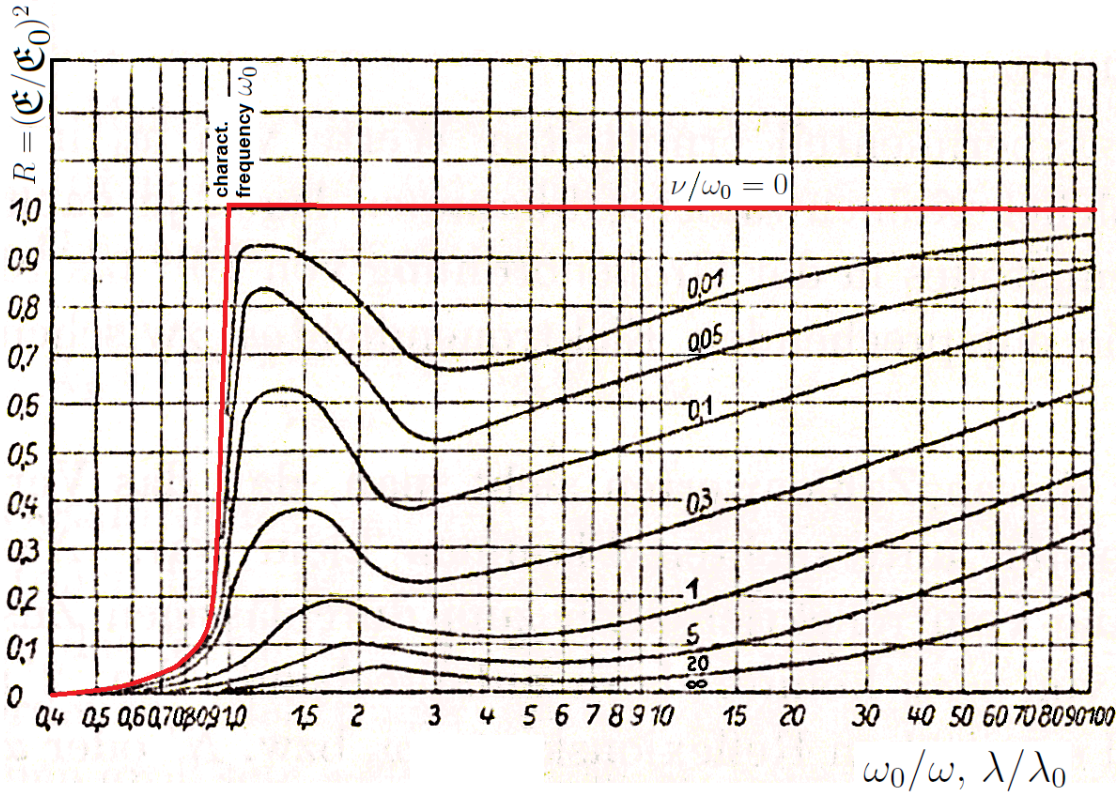



Figure 2: Reflectivity $R$ of a gas column with a mixing zone thickness of $s_m = \lambda_0/10$ (distance from the nozzle opening $l = 5.7 \cdot \lambda_0$), relative collision number of the unmixed zone $\nu/\omega_0$ as parameter

of the alternating field. On the other hand, the occurrence of the so-called Luxemburg effect based on this can be used to experimentally determine the average collision number in a flame.

The effective radius $r_i$ in Equation 10 depends not only on the electron velocity but also on the degree of molecular excitation. A very accurate calculation of the collision frequency $\nu$ is therefore not possible for most combustion processes. However, since it is not the absolute value of $\omega_0$ or $N'$, but only the accuracy with which these values can be determined at a specific point in a flame that depends on $\nu$, it is sufficient in this case to estimate the order of magnitude of $\nu$. For this purpose, we can assume, for example, in the case of hydrocarbon combustion, by extrapolation from measurements of Ramsauer, [2], that the effective radius of the molecules occurring in the flame is approximately 1.5 Å. At normal pressure, depending on the temperature of the location under consideration, the electron collision numbers are then between $1 \times 10^{10}$ and $1 \times 10^{11}$ per second.

The experimentally determined values of $\omega_0$ in the reaction zone of such

hydrocarbon flames were in the range of $1 \times 10^{10}$ and $1 \times 10^{12}$ per second, depending on the calorific value of the fuel, and the corresponding electron densities were between $1 \times 10^{11}$ and $1 \times 10^{14}$ per cubic centimeter.

These numerical values show that the ratio $\nu/\omega_0$ was small for most of the flames investigated. From the sharp transition from the reflective to the transparent state for small values of $\nu/\omega_0$, $\omega_0$ or $N'$ or $\alpha_i$ could then be determined with a high degree of accuracy from the experimentally determined reflection curve, as shown in Figure 2.

As the temperature decreases, $\nu$ increases proportionally to $\sqrt{T}$ according to Equation 10. The electron density decreases approximately proportionally to $T^{3.5}$ as the temperature decreases. As the distance from the reaction zone increases, $\nu/\omega_0$ therefore increases very rapidly and the accuracy of the reflection measurement method decreases accordingly.

The validity of dispersion theory for ionized gases, which has been largely confirmed by research of the ionosphere, makes it unlikely that the reflection measurement method based on it will yield ionization degrees that are too high by orders of magnitude in flames. In the following section, we will now examine what sources of error could lie in the classical calculation method for thermal ionization, since, as already mentioned in the introductory section, this method yields significantly lower degrees of ionization than those measured using the reflection method.

# 3. Calculation of the Degree of Ionization of Flames according to Saha's Equation

With complete energy equilibrium, [9, 26], thermal ionization can be understood as a chemical dissociation process according to the equation

$$\text{atom} \;=\text{ion}\; +\; \text{electron-ionization work}\,.$$

This assumes that the number of electrons released is equal to the number of ions formed. This assumption is valid for combustion processes because the energy required to split off a second valence electron is significantly greater than that required for the first, meaning that the probability of multiple ionization remains very low.

According to the law of mass action, the equilibrium constant $k_p$ and the degree of ionization $\alpha_i$ of a chemically uniform gas, are related via the formula

$$k_p = \frac{f_{\text{ion}} \cdot p_{\text{ion}} \cdot f_{\text{el}} \cdot p_{\text{el}}}{p_{\text{atom}}} = f_{\text{ion}} \cdot f_{\text{el}} \cdot p \cdot \frac{\alpha_i^2}{\left(1-\alpha_i^2\right)}\,, \tag{11}$$

where $p$ is the total pressure, $p_{\text{el}}$, $p_{\text{ion}}$, and $p_{\text{atom}}$ are the partial pressures of the electrons, ions, and neutral particles of the ionized gas, respectively.

Furthermore, $\alpha_i$ represents the ratio of the number of ionized particles or released electrons (the number of which should be equal according to the above assumption) to the number of originally present neutral molecules. $f_{\text{ion}}$ and $f_{\text{el}}$ are so-called activation coefficients, which must be multiplied by the concentrations or partial pressures of charge carriers in order to preserve the law of mass action. They become equal to one when the degree of ionization is zero and decrease as the degree of ionization increases.

On the other hand, according to EGGERT, the equation

$$\begin{aligned} k_p &= (k_{\text{B}}T)^{2.5} \cdot \left(\frac{2\pi \cdot m_{\text{el}}}{h^2}\right)^{1.5} \cdot e^{-\frac{W_0}{k_{\text{B}}T}} \\ &= 1.43 \times 10^{57} \cdot (k_{\text{B}}T)^{2.5} \cdot e^{-\frac{W_0}{k_{\text{B}}T}} \end{aligned} \tag{12}$$

can be derived from the VAN'T-HOFF equation with sufficient accuracy for the value of the equilibrium constant $k_p$ as a function of temperature. In this equation, $W_0$ is the ionization energy for the first valence electron per molecule, m kg, $m_{\text{el}}$ is the mass of an electron, kg s$^2$ m$^{-1}$, $k_{\text{B}}$ is BOLTZMANN's constant, m kg $^{\circ -1}$, and $h$ is PLANCK's constant, m kg s.

The following assumptions were made when deriving this equation:

1. The thermodynamic constants for ions and neutral molecules are equal.
2. The electron corresponds in its properties to a monatomic molecule with a correspondingly small molecular weight.
3. The pressure dependence of the equilibrium constant $k_p$ above approximately $p = 30.4$ bar is neglected (according to EUCKEN, [12], at higher pressures the value $\log(k_p)$ decreases approximately linearly with increasing pressure).

From Equation 11 and Equation 12 and the further approximation assumption $f_{\text{ion}} \cdot f_{\text{el}} = 1$, we then obtain the so-called SAHA equation:

$$\frac{\alpha_i^2}{\left(1-\alpha_i^2\right)} = 4.707 \times 10^{55} \cdot \frac{(k_{\text{B}}T)^{2.5}}{p} \cdot e^{-\frac{W_0}{k_{\text{B}}T}} \tag{13}$$

or in the notation more familiar to engineers:

$$\frac{\alpha_i^2}{\left(1-\alpha_i^2\right)} = 4.84 \times 10^8 \cdot \frac{U_i^{2.5}}{p} \cdot \vartheta^{2.5} \cdot e^{-\frac{1}{\vartheta}} \tag{14}$$

or

$$\frac{\alpha_i^2}{\left(1-\alpha_i^2\right)} = \frac{B}{p} \cdot \vartheta^{2.5} \cdot e^{-\frac{1}{\vartheta}}\,. \tag{14'}$$

In Equation 14' the symbols have the following meanings: $\vartheta \equiv \frac{k_{\text{B}}T}{eU_i}$, $B \equiv 4.73 \times 10^3 \cdot U_i^{2.5}$, $e$ is the elementary charge in C, $U_i$ is the ionisation current

| type of gas | $U_i$, volt | $\vartheta/T \cdot 10^6$ | $B \cdot 10^6$ |
|---|---|---|---|
| $H_2O \leftrightarrow {}_2O^+ + e^-$ | 13.0 | 6.63 | 2.82 |
| $CO_2 \leftrightarrow O\text{–}C\text{–}O^+ + e^-$ | 14.4 | 5.98 | 3.74 |
| $CO \leftrightarrow CO^+ + e^-$ | 14.1 | 6.11 | 3.55 |
| $OH \leftrightarrow OH^+ + e^-$ | 11.6 | 7.43 | 2.16 |
| $O_2 \leftrightarrow O\text{–}O^+ + e^-$ | 12.5 | 6.90 | 2.60 |
| $H_2 \leftrightarrow H\text{–}H^+ + e^-$ | 15.8 | 5.45 | 4.73 |
| $O \leftrightarrow O^+ + e^-$ | 13.57 | 6.35 | 3.18 |
| $H \leftrightarrow H^+ + e^-$ | 13.54 | 6.36 | 3.14 |

Table 1: Ionization voltages, $\vartheta/T$ and $B$ of different types of molecules

| cross section | $d_0$ | $d'$ | $d_m$ |
|---|---|---|---|
| diameter, m | 0.950 | 0.403 | 0.700 |
| pressure $p$, $\mathrm{kg\,cm^{-2}}$ | 16.7 | 9.25 | 1 |
| temperature $T$, $^\circ$K | 2820 | 2520 | 1605 |

Table 2: Data for calculating the theoretical curve in Figure 4

in V and $p$ the prssure in $\mathrm{kg\,cm^{-2}}$.

For the main types of molecules occurring in the flames examined using the reflection measurement method, the values of the ionization voltage $U_i$, as well as the constants $\vartheta/T$ and $B$, are summarized in the following Table 1. Using these values, the theoretical curve of the ionization degree $\alpha_i$ and the electron concentration $N'$ per cubic centimeter along a rocket similar to type $V_2$, as shown in Figure 3, was plotted in Figure 4 using the data listed in Table 2 for normal hydrocarbon-oxygen combustion. The assumption was that the SAHA equation applies without restriction in every cross-section of the rocket.

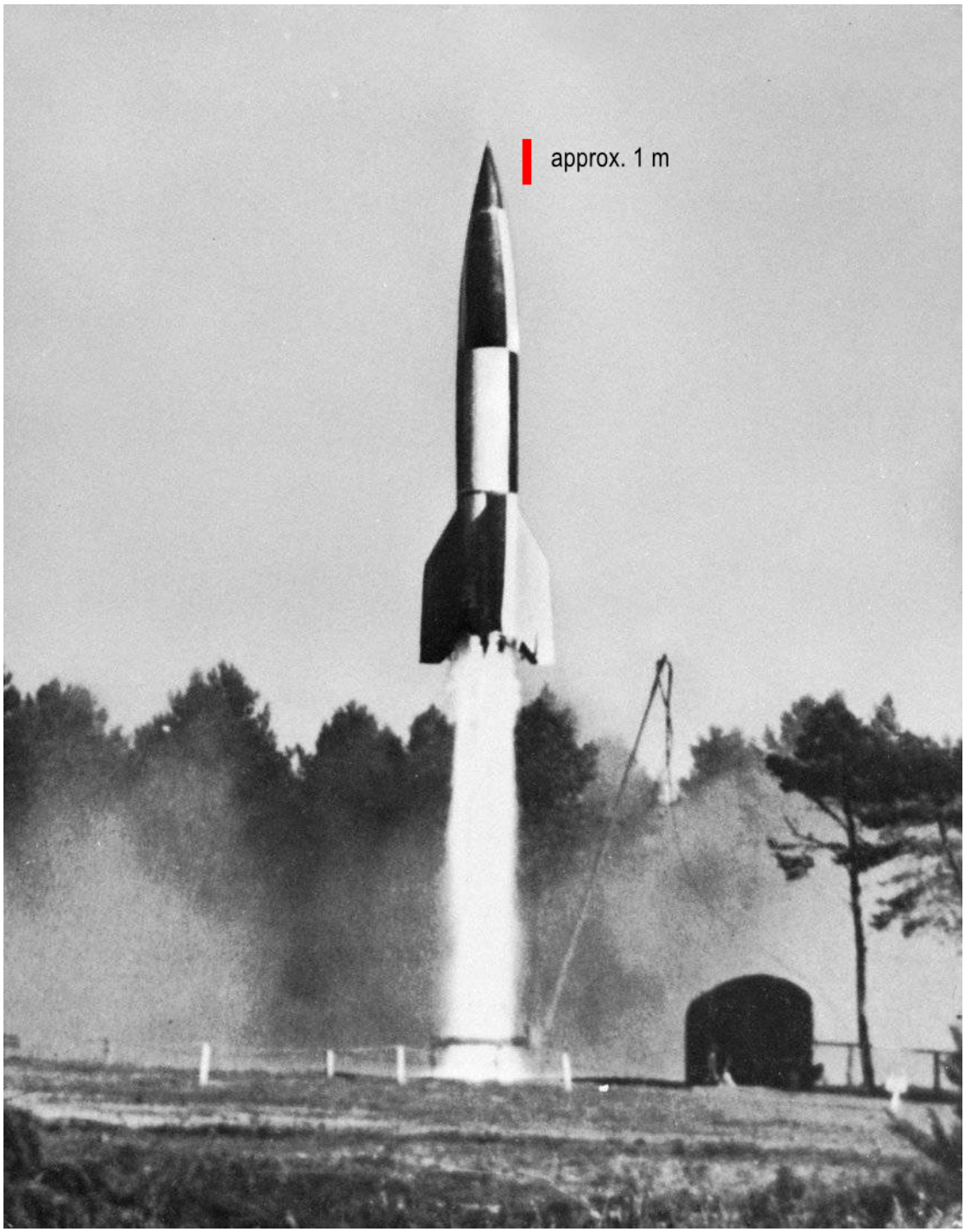



Figure 3: Launch of $V_2$ rocket in Peenemünde WW2, 1944

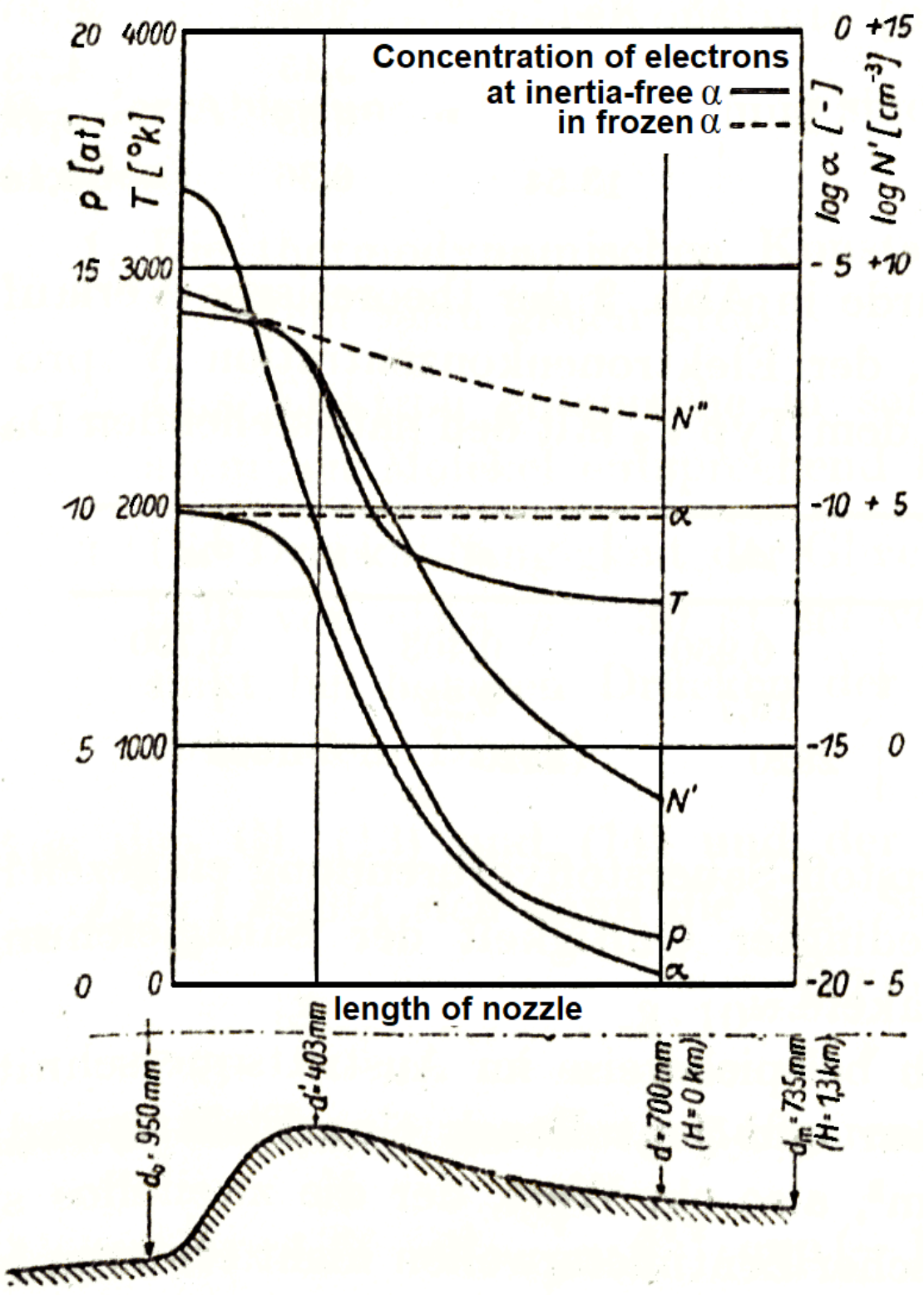



Figure 4: Temperature $T$, pressure $p$, ionization degree $\alpha$, and number of electrons per cubic centimeter $N'$ of a $V_2$-like rocket, assuming the validity of the SAHA equation

This results, for example, in an electron density of 0.08 electrons per cubic centimeter in the exit cross section $d_m$ at a gas temperature of 1605 °K and a pressure of 1.013 bar. This value cannot explain the reflection of centimeter waves, which undoubtedly occurs, since electron densities of more than $1 \times 10^{11}$ electrons per cubic centimeter are necessary for the reflection of such waves with such a small wavelength.

If we allow for a certain degree of delay in the reversal of the ionization that has occurred and consider the maximum ionization inside the combustion chamber ($d_0$) at 2820 °K and 16.9 bar, the SAHA equation yields an electron density of $3.3 \times 10^9$ per cubic centimeter. If the degree of ionization remains constant, taking into account the changes in pressure and volume, this would result in an electron density of $3.5 \times 10^8$ electrons per cubic centimeter for the measuring point at the outlet cross-section ($d_m$). This maximum possible value, calculated using the classical method, does not take into account the considerable losses of free electrons due to the sharp increase in recombination as the temperature decreases. Nevertheless, this value of $3.5 \times 10^8$ electrons per cubic centimeter is not sufficient to explain the measured centimeter wave reflection.

Before attempting a more in-depth explanation, we should briefly assess the possible influence of the neglected activation coefficients on the calculation results. These values, assumed in calculation 1, become smaller as the ion concentration increases, so that when they are taken into account, the actual degree of ionization must be higher than the values given by the SAHA equation. These coefficients take into account the force between the electrically charged particles, and their magnitude therefore depends on the charge, the distance, and the effective radius of the ions (or electrons). Theoretical and metrological investigations of the magnitude of the activation coefficients as a function of the degree of ionization seem to be available only in the field of electrolyte solutions. Here, for example, in the region of very dilute solutions according to DEBYE-HÜCKEL, the equation

$$\log(f) = -0.505 \cdot \sqrt{c_0}\,,$$

applies to a single ionization with the formation of two oppositely charged ions, where $c_0$ represents the total concentration of the electrolyte in moles/liter. The same average ion distances as an electrolyte solution with a concentration of $c_0 = 1\,\mathrm{mol\,L^{-1}}$ would have an ion concentration of approximately $6 \times 10^{20}$ particles per cubic centimeter in the gas plasma. If it is permissible to extend the laws governing electrolyte solutions to gas plasmas, an ion concentration of $1 \times 10^{11}\,\mathrm{cm^{-3}}$ would only correspond to around $2 \times 10^{-10}\,\mathrm{mol\,L^{-1}}$ and would therefore not result in activity coefficients that deviate significantly from 1. However, the ion and electron densities that have appeared in the calculation so far are all still below this value.
Since all the variables used in the SAHA equation to calculate the degree of ionization in flames are known with sufficient accuracy so that deviations

in magnitude between the calculation and the measurement results cannot be explained by the insufficiently known magnitude of individual numerical values according to the equally well-founded dispersion theory, it seems reasonable to assume that the cause of the significant deviation between the calculation and the measurement results is that the prerequisite for the validity of the SAHA equation, namely a stable established equilibrium, was not met in the flames investigated and presumably does not apply to flames in general.

# 4. Approach for Calculating the Degree of Ionization, Taking into Account the Non-Inertia-less Establishment of Equilibrium States

An explanation as to why the SAHA equation, which is based on equilibrium conditions, is unlikely to provide accurate results for combustion processes will be attempted with the aid of a schematic overview of the combustion process.
For this purpose, it is assumed that in such a process, the total amount of energy supplied by the calorific value of the fuel is kept constant for the period of equilibration of the various degrees of freedom by means of appropriate insulation, i.e., the process is adiabatic. Based on the results of known research to be found in [18, 13, 27, 19, 17, 22, 4, 5, 1], it can be assumed for some estimates that the necessary collision numbers for establishing thermal equilibrium after a significant change in the state of the gases behave progrediently as illustrated in Table 3.

| translation | rotation | vibration | dissociation | ionization |
|---|---|---|---|---|
| $1 \times 10^1$ | $1 \times 10^3$ | $1 \times 10^5$ | $1 \times 10^7$ | $1 \times 10^9$ |

Table 3: Ratio of collision numbers for different types of gas particle dynamics

The usual equilibrium relationships, the law of mass action, the SAHA equation, etc., describe a state in which the same number of partners are created as disappear in a unit of time. They can therefore only be legitimately applied to gases in which at least $1 \times 10^7$ collisions per particle have occurred since the change of state, i.e., in the case of dissociation phenomena, or at least $1 \times 10^9$ collisions, if ionization equilibria (under certain temperature conditions) are predominant. In rockets, the residence times are usually sufficient to establish dissociation equilibria in the combustion chamber. For nozzle flow, they are often insufficient for dissociation equilibria and, overall, far from sufficient for ionization equilibria.
The following very schematic representation of the processes leading to ionization during combustion can be imagined, which is modified accordingly by the mechanism of chain reactions:
In any case, the initial state of the combustion gases is the same as immediately after the chemical reaction, in which the total reaction energy $E$ is present as undistributed translational energy. The molecular velocity of the newly formed particle is therefore

$$c_1 = \sqrt{\frac{2g \cdot E}{A}}\,, \tag{15}$$

where $g$ is the acceleration due to gravity and $1/A$ is the mechanical heat equivalent. For a rocket operating with stoichiometric hydrocarbon-oxygen combustion at a mixture heating value of $E = 10\,831\,\mathrm{kJ\,kg^{-1}}$, $c_1 = 4640\,\mathrm{m\,s^{-1}}$ would apply, for example.
Since the ionization energies $E_i$ of the molecules involved in hydrocarbon-oxygen combustion are between $32.5\,\mathrm{MJ\,kg^{-1}}$ to $46.1\,\mathrm{MJ\,kg^{-1}}$, minimum particle velocities of $8050\,\mathrm{m\,s^{-1}}$ to $9600\,\mathrm{m\,s^{-1}}$ are required for this energy if translational collisions of molecules are initially assumed to be the cause of the formation of free electrons during thermal ionization. This initial state of undistributed translational energy with a particle velocity of $4640\,\mathrm{m\,s^{-1}}$ cannot yet lead to ionization.

According to Table 3, the first equilibrium conditions will be that of the Maxwell distribution of this pure translational energy during the first 10 collisions. According to Boltzmann, this distribution corresponds to a translational temperature $T_l$ of

$$T_l = \frac{2}{3} \cdot \frac{EM}{\mathscr{R}}\,, \tag{16}$$

where $M$ is the molecular weight and $\mathscr{R}$ is the universal gas constant. For the above example, this "translational temperature" with the values for $M \approx 30\,\mathrm{kg\,mol^{-1}}$ and $\mathscr{R} \approx 8.374\,\mathrm{kJ\,mol^{-1}\,{}^{\circ}{}^{-1}}$ is approximately $T_l \approx 10E = 25\,870\,^{\circ}\,\mathrm{K}$. The mean particle velocity is given by the translational equilibrium condition according to

$$c_2 = c_1 = \frac{2gE}{A} = \sqrt{\frac{3g\mathscr{R}T_l}{MA}} \tag{17}$$

for the example, i.e., again $c_2 = c_1 = 4640\,\mathrm{m\,s^{-1}}$.

In addition to this mean molecular velocity, the Maxwell distribution of this second state is known to include all molecular velocities between 0 and $\infty$, i.e., also those above the ionization velocities $c_i = 8050\,\mathrm{m\,s^{-1}}$ to $9600\,\mathrm{m\,s^{-1}}$ required to ionize an unexcited particle.

The weight fraction of gas particles $N'$ that are faster than $c_i$, and for which ionization would therefore be expected under favorable conditions, is approximately

$$\frac{N'}{N} = \sqrt{\frac{6}{\pi}} \cdot \frac{c_i}{c_1} \cdot e^{-\frac{3}{2}\cdot\left(\frac{c_i}{c_1}\right)^2}\,. \tag{18}$$

for large values of $c_i/c_1$. For our example of a hydrocarbon rocket, $N'/N = 0.6 \times 10^{-2}$, in the combustion gases of a $V_2$ rocket with alcohol combustion, with $E = 6448\,\mathrm{kJ\,kg^{-1}}$ and $c_1 = 3590\,\mathrm{m\,s^{-1}}$, the quotient $N'/N =$ would be $0.16 \times 10^{-2}$. With a 100 % yield of the few collisions available for ionization, the degree of ionization would thus be determined. The share of the total energy attributable to ionization would be 3.2 % for the rocket in our example

and approximately 0.1 % for the $V_2$ rocket.
As the number of collisions continues to increase, the pure translational energy considered so far is distributed among more and more degrees of freedom, while maintaining MAXWELL's velocity distribution in accordance with the above collision number ladder in Table 3. This proceeds until the known dissociation equilibrium temperature is reached after $1 \times 10^7$ collisions, which for the rocket in this example is $T_a = 3700\,^\circ\,\mathrm{K}$ at a furnace pressure of 101.3 bar. This corresponds to a mean molecular velocity of $c_3 = \sqrt{3g\mathscr{R}T/AM} = 1760\,\mathrm{m\,s^{-1}}$. The weight fraction of gas particles that are now faster than $c_i$ is now approximately $N'/N = 3.5 \times 10^{-3}$ and is approaching the values provided by the SAHA equation.

During the process of equilibrium of the individual degrees of freedom (apart from photoionization), the portion of the translational velocity exceeding the minimum ionization velocity can lead to ionization until, after $1 \times 10^2$ collisions, all equilibria have been established and thus also the equilibrium temperature underlying the SAHA equation has been reached. The energy balance of this schematic combustion process is shown in Figure 5. From this, in conjunction with Equation 18, it can be seen that once rotational equilibrium has been established, the probability of further ionization collisions becomes negligible. The vast majority of all free electrons would therefore have to be formed during the first $1 \times 10^2$ collisions after the reaction.

Given a specified steady flow velocity of the flame, the collision number according to Figure 5 is also a certain measure of the distance of the particles under consideration from the reaction zone, in which the equilibration of the relevant degree of freedom can be expected. From the course of pressure, temperature, and steady flow velocity as a function of the streaming trajectory, it can be seen, for example, that at the measuring point mentioned in section 2, a particle can have undergone a maximum of $1 \times 10^6$ collisions on average since the reaction took place. Accordingly, the SAHA equation cannot yet be valid for this point, because the prerequisite of equilibration between ionization and recombination (which requires approximately $1 \times 10^9$ collisions under the temperature and pressure conditions present here) is unlikely to have been met.
Equation 18 initially only provides information about the proportion $N'$ of the total number of particles $N$ that can lead to ionization after the translational equilibrium has been established. To the same extent that translational energy is converted into ionization energy by ionization collisions, there is a continuous readjustment of the MAXWELL distribution for the translational energy and replenishment of its depleted end range (red shaded area in Figure 6) of fast particles, so that new particles are constantly becoming capable of ionization until the sharp drop in the translational energy level due to the rotation equilibration becomes noticeable. Thus, in the course of the first $10^1$ collisions, a multiple of the particle number expressed by Equation 18 will reach the minimum energy for ionization.

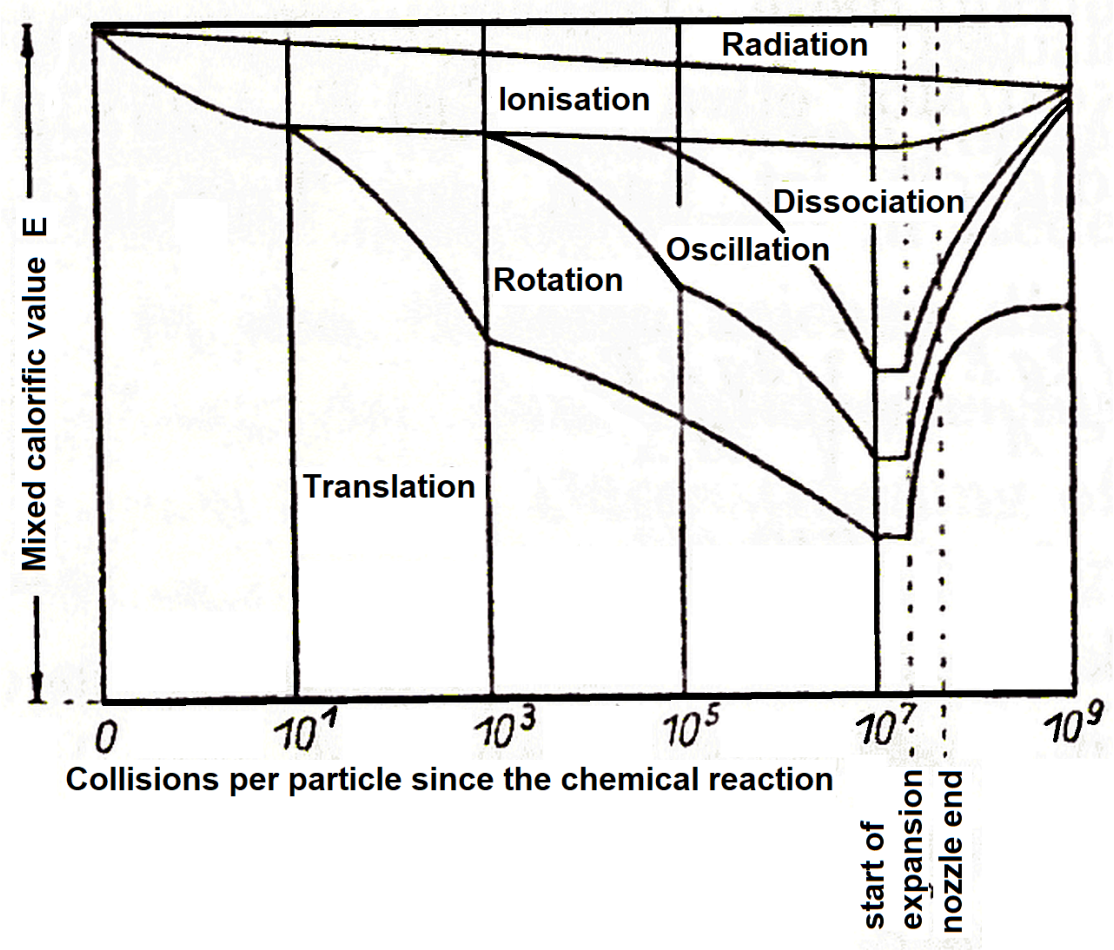



Figure 5: Schematic diagram of the process of equilibrium in the combustion gases of the rocket considered in the example

The free electrons formed also assume an approximate MAXWELLian velocity distribution (at least at low ionization levels), so that ionization by electron collisions can also be expected.

As a result of cumulative excitation, i.e., collisions with molecules that are already excited, it is possible that some collisions may result in ionization with a kinetic energy that is lower than the ionization energy from the ground state. This initially results in a probability for degrees of ionization that are significantly higher than the result of Equation 18.
On the other hand, it is not to be expected that every collision of a particle with kinetic energy exceeding the ionization energy will also lead to ionization. For example, the energy and momentum conservation laws for a central, inelastic collision with approximately equal masses of the colliding partners imply that the original kinetic energy of the colliding particles must be

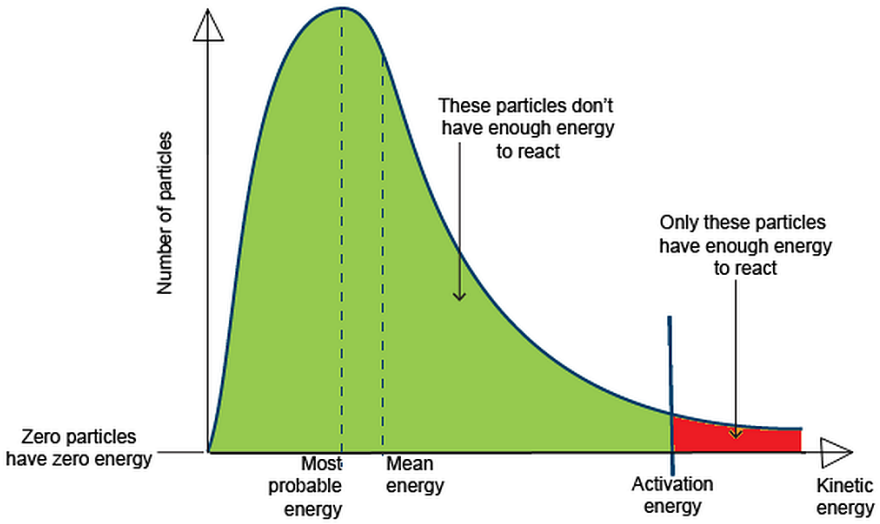

Number of particles
These particles don't have enough energy to react
Only these particles have enough energy to react
Zero particles have zero energy
Most probable energy
Mean energy
Activation energy
Kinetic energy

Figure 6: Maxwell–Boltzmann distribution curve according to [23]

equal to twice the ionization energy if ionization is to occur while conserving momentum. According to the Maxwell distribution, the proportion of particles with double the ionization energy is only a very small fraction of the particles according to Equation 18. In electron collisions, on the other hand, the basic ionization energy is a sufficient condition due to the large mass difference.
The mathematical recording of all these processes poses great difficulties even in the simplest combustion processes, such as hydrogen combustion. In the combustion of hydrocarbons, there is the additional problem that the sequence of the individual, highly complex chain reactions is not yet sufficiently understood.

If we base the calculation of the highest degree of ionization of a flame, namely that of the reaction zone, on Equation 18 and take into account all the processes mentioned above, which cannot yet be calculated in detail, by means of an additional "current efficiency factor", this factor is in the order of a few percent. The latter depends on the type of fuel, in order to ensure consistency between the calculation and the measurement. This value is roughly consistent with the current efficiency factors for electrical gas discharges.

Due to a lack of experimental facilities, the authors have not yet been able to determine the current efficiency factor more precisely.
The ionization of a flame therefore initially depends only on the calorific value $E$ of the mixture of the fuel, and not on the operating conditions, i.e., in the case of a rocket, not on the furnace pressure, relaxation state, etc. These results are also consistent with the previous results of reflection

measurements with centimeter waves on rocket exhaust gases, which were carried out by one of the authors. These measurements showed that the electron concentrations were essentially only dependent on the calorific value of the fuels, but were hardly influenced by the combustion chamber pressure in the range of 1 bar to 152 bar. This initially unexpected result lends a high degree of probability to the above ideas about the behavior of combustion gases.

# 5. The Calculation of Chemiluminescence of Flames based on States of Non-equilibrium

The order of magnitude agreement between the ionization degrees calculated in this way and the values measured using radio technology may now encourage us to apply the analog mechanism to the calculation of chemiluminescence as well.

All collisions in the MAXWELL distribution of pure translational equilibrium, i.e., the second state defined in the previous section, that occur more slowly than the ionization rate will apparently only lead to radiation excitation as long as there have not yet been enough collisions for the rotational, vibrational, and dissociation equilibria to be established. In the case of electron excitations, these are known to decay after about $1 \times 10^{-8}$ s, i.e., in our example after about $1 \times 10^3$ collisions under light quantum emission, if they have not been damped beforehand by collisions of the second type.
While the equilibrium radiation of the combustion gases occurs predominantly in the long-wave infrared radiation range, the chemiluminescence of the type considered here lies in the short-wave ultraviolet range with wavelengths up to at most the beginning of the infrared range ($O^2$-lines, for example, up to about 4000 Å). This corresponds to minimum energy amounts of about $10\,\mathrm{MJ\,kg^{-1}}$ or collision velocities of $c_e = 4470\,\mathrm{m\,s^{-1}}$.

The proportion of molecules in state 2 that are eligible for luminescence therefore lies in the velocity range between $c_e = 4470\,\mathrm{m\,s^{-1}}$ and $c_i = 9150\,\mathrm{m\,s^{-1}}$ and amounts to

$$\begin{aligned}\xi &= \frac{N_e}{N} \\ &= \sqrt{\frac{6}{\pi}} \cdot \left\{ \frac{c_e}{c_1} \cdot e^{-\frac{3}{2}\cdot\left(\frac{c_e}{c_1}\right)^2} - \frac{c_i}{c_1} \cdot e^{-\frac{3}{2}\cdot\left(\frac{c_i}{c_1}\right)^2} \right\} \\ &+ \frac{2}{\sqrt{\pi}} \cdot \int_{x=\sqrt{3/2}c_e/c_1}^{\sqrt{3/2}c_i/c_1} e^{-x^2}\,\mathrm{d}x\,, \end{aligned} \tag{19}$$

In our example of a rocket with hydrocarbon-oxygen combustion, $N_e/N =$

0.42, i.e. 42 % of the mass turnover of the combustion. The energy radiation of the rocket is $0.42 \cdot 10006/10831 = 38.8\,\%$ of its energy conversion if all molecules in question actually transform into radiation and exhibit a radiation limit of approximately 4000 Å.
In practice, the time between two collisions is usually shorter than the lifetime $\tau$ of an excitation, which is calculated according to

$$\tau = \frac{3cm}{8\pi^2 e^2} \cdot \nu^{-2} = 44975.814 \cdot \lambda^2 \text{ in seconds} \tag{20}$$

where $c$ is the speed of light, $m$ is the rest mass of the electron, $e$ is the elementary charge, $\nu$ is the frequency, and $\lambda$ is the wavelength in meters.

A particle can therefore continuously emit the frequency $\nu = c/\lambda$ in the limiting case. This allows us to find a simple transition from the radiation quantum $\varepsilon = h \cdot \nu$ to the radiation intensity $J_0$ by introducing the optically effective molecular cross section $Q = \pi \cdot r_0^2$. This results in

$$J_0 = \frac{\varepsilon}{Q} \cdot \tau\,. \tag{21}$$

If the molecule radiates simultaneously by means of a larger number of additional excitation collisions, the intensity can be increased by one or two orders of magnitude. On the other hand, the current efficiency factor discussed in section 4 regarding ionization can reduce the intensity by similar orders of magnitude, so that one is inclined to start with the simple Equation 19.

Using the numerical values from our example in

1. $\varepsilon = 5.07 \times 10^{20}$ m kg,
2. $Q = 5 \times 10^{-23}$ m$^2$,
3. $\tau = 0.72 \times 10^{-3}$ s[3]

we obtain a radiation power of $J_0 = 1.41 \times 10^{11}$ m kg m$^{-2}$ s$^{-1}$ or $1.382 \times 10^9$ kJ m$^{-2}$ s$^{-1}$. This is around $10^5$ times more than the blackbody radiation at the equilibrium temperature of 3700 ° K would correspond to.

If we consider the known total luminescence radiation power of a high-pressure rocket with an energy conversion of $3.571 \times 10^6$ kJ s$^{-1}$, i.e., a luminescence radiation with the intensity $0.388 \cdot 3\,571\text{e}6 = 1.386 \times 10^6$ kJ s$^{-1}$ concentrated on a surface, its size is only $1.386 \times 10^6 / 1.382 \times 10^9 = 1 \times 10^{-3}$ m$^2$, which corresponds, for example, to a sphere with a diameter of 4 cm.

The radiation from this sphere is absorbed in its environment by all the atoms and molecules present, with an effective molecular radius of approximately $r_0 = 0.4 \times 10^{-11}$ m and a particle number of $n = 1.92 \times$

[3]Corresponds to a wavelength of approximately 127 µm if calculated with Equation 20.

$10^{26}\,\mathrm{m}^{-3}$, i.e. an absorption constant $a = n \cdot r_0^2 \cdot \pi = 0.96 \times 10^4\,\mathrm{m}^{-1}$. According to the absorption law

$$\frac{J}{J_0} = 1 - e^{-a \cdot s}$$

the radiation intensity therefore decreases extremely rapidly with distance $s$ from the surface of this radiation center and becomes weaker than the equilibrium radiation of carbon dioxide and water vapor within distances of millimeters.

A combustion gas is therefore completely isolated from short-wave and locally concentrated luminescence radiation. The radiation can only become dangerous to a combustion chamber wall if it comes into direct contact with it. This is consistent with practical experience, which shows that the reaction zones of combustion gases should be located as far away from the furnace walls as possible, towards the interior of the furnace. However, the danger posed by luminescent gas particles near the walls of a high-pressure combustion chamber is greatly reduced in practice by steady flow and temperature boundary layers.

The extraordinary radiation density of the high-pressure combustion gas allows practically negligible amounts of chemiluminescence to escape to the outside. Similar to the high translation temperatures of states 1 and 2, it serves only to rapidly establish energy equilibria, i.e., it further promotes this molecular collision process through photon collisions.

In such combustion systems, the extraordinary intensity of chemiluminescence causes the injected fuel droplets to vaporize very rapidly over very short distances, thus easily explaining the rapid mixture creation in liquid rockets, which previously could not be explained by heat transfer through convection, diffusion, and equilibrium radiation alone. Finally, it should be noted that in combustion systems with very low combustion gas density, such as ramjet engines, the absorption coefficients can be several orders of magnitude lower than in the example used here, which means that the combustion gas can then also become transparent to luminescence radiation. As a result, this begins to contribute noticeably to wall heating, as is well known from practical experience. In this case, the droplets of the injected fuels are also noticeably heated over greater distances. If, in addition, combustion with air is involved, the intensity of the luminescence itself drops considerably, e.g., from the previously calculated value of $1.382 \times 10^9\,\mathrm{kJ\,m^{-2}\,s^{-1}}$ to about $8.122 \times 10^6\,\mathrm{kJ\,m^{-2}\,s^{-1}}$. However, it still remains more than four orders of magnitude higher than the corresponding equilibrium radiation of water vapor-carbon dioxide (see also section 2).

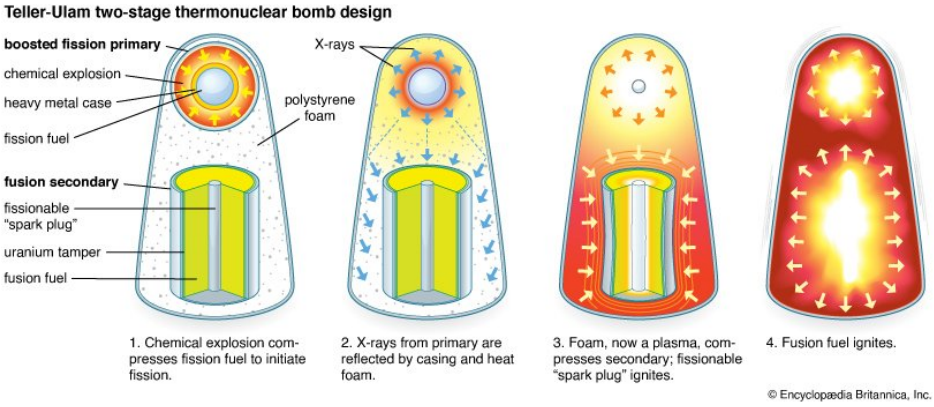
# 6. Final Conclusion

The present hypothesis on the origin and calculation of ionization and chemiluminescence in flames represents a very preliminary attempt to explain and quantitatively record these phenomena. In particular, the numerical data may still be subject to considerable correction. The authors are well aware of the boldness of some of their assumptions and also that further experimental investigations would be necessary to shed more light on the individual processes. Since the authors themselves currently lack the opportunity to conduct such experimental investigations, they considered it appropriate to present their views, which are based on only sparse observations, to the scientific community in order to encourage further observations and experiments.

# Part II.
# On the Problem of Chemical Ignition of Thermal Nuclear Reactions

# On the Problem of Chemical Ignition of Thermal Nuclear Reactions

By E. Sänger.


Teller-Ulam two-stage thermonuclear bomb design
boosted fission primary
chemical explosion
heavy metal case
fission fuel
fusion secondary
fissionable "spark plug"
uranium tamper
fusion fuel
X-rays
polystyrene foam
1. Chemical explosion compresses fission fuel to initiate fission.
2. X-rays from primary are reflected by casing and heat foam.
3. Foam, now a plasma, compresses secondary; fissionable "spark plug" ignites.
4. Fusion fuel ignites.
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**Abstract**

The ignition temperatures of thermal nuclear reactions are seven to ten orders of magnitude higher than those of conventional chemical combustion reactions and five to eight orders of magnitude higher than the highest chemical reaction temperatures.
At the center of converging compression shock waves in gases, the temperature theoretically rises towards infinity.
Newer views on the nature of the detonation of solid and liquid explosives allow their detonation waves to be understood as compression shocks in the explosive gasified by luminescence radiation, which are followed by the chemical reaction.
With the help of such convergent detonation waves, it is therefore possible to increase the temperature of a finite fraction of the chemically reacting explosive mass to the range of thermal core ignition temperatures.
The limit of this dynamic temperature increase is determined by the total ionization temperature, and mixtures of explosive vapors with the highest total ionization temperature and the lowest core ignition temperature appear to approach critical conditions.

# 1. Introduction

In accordance with Part I, [30, 32], we start from a number of observations concerning ionization and luminescence in flames, from a hypothesis based on these observations concerning the combustion of nitroglycerin powders, [29], and the theory of strong spherical and cylindrical compression shocks near the center of the sphere or the axis of the cylinder, [16].
We apply the model concept of the powder combustion hypothesis to the detonation of any solid or liquid explosives, including non-classical explosives. We do this by assuming that when the detonation front passes through the explosive, it is initially melted, vaporized, and converted into a reactive gas mixture by the intense luminescence of the reaction zone behind the shock front.
This fresh gas mixture is further compressed in a non-isentropic manner by a strong, initially plane compression shock, which, based on experience, advances at speeds of the order of $1 \times 10^4\,\mathrm{m\,s^{-1}}$. The fresh gas mixture is heated to a high temperature so that immediately after the shock, the reactive mixture ignites and burns out very quickly due to the high temperatures and ideal mixture.
In chronological order, the phases of detonation experienced by an explosive particle are as follows: (i) vaporization and preparation, (ii) compression shock, (iii) combustion. Some very rough estimates may illustrate this picture:

With a specific weight of the explosive of $\gamma_1 = 1600\,\mathrm{kg\,m^{-3}}$ and a temperature of the processed but not yet ignited vaporization products of $T_1 \sim 400\,^\circ\mathrm{K}$ at a molecular weight of $M_1 \sim 20$, the initial pressure of the fresh gas between the solid explosive surface and the compression shock is approximately

$$p_1 \sim \gamma_1 \cdot \frac{\mathscr{R}\,T_1}{M_1} = 2.7 \times 10^7\,\mathrm{kg\,m^{-2}} = 2700\,\mathrm{at} \tag{22}$$

We now think of the fresh gas with the state variables $p_1$, $\rho_1$, $T_1$, $M_1$ and the speed of sound $a_1 \sim 460\,\mathrm{m\,s^{-1}}$ with a velocity $v_1 \sim 10\,000\,\mathrm{m\,s^{-1}}$, i.e., a MACH number of the flow of $\frac{v_1}{a_1} \sim 22$ streaming against the front of the compression shock.

# 2. Theoretical Considerations

In the known relationships of the planar compression shock for the pressure and temperature increase according to the equations

$$\frac{p_2}{p_1} = 1 + \frac{2\varkappa}{\varkappa+1} \cdot \left( \left[\frac{v_1}{a_1}\right]^2 - 1 \right), \tag{23a}$$

$$\frac{T_2}{T_1} = 1 + \frac{2\varkappa}{\varkappa+1} \cdot \left( \left[\frac{v_1}{a_1}\right]^2 - 1 \right) \cdot \frac{\varkappa-1}{\varkappa+1} \cdot \left( 1 + \frac{1}{\varkappa \cdot \left[\frac{v_1}{a_1}\right]^2} \right), \tag{23b}$$

the value of $\varkappa$ for monatomic gases, $\varkappa = 1.67$, must be used. On the one hand, because the molecules could be largely dissociated. In any case, however, because the inertiæ of the internal degrees of freedom during the very short actual collision process only allow for an adjustment of the translational movements, meaning that the specific heats also remain constant up to arbitrarily high temperatures.
Under this assumption, we obtain, for example, $\frac{p_2}{p_1} = 605$, i.e., $p_2 \sim 1.63 \times 10^6\,\mathrm{at}$ and $\frac{T_2}{T_1} = 153$, i.e. $T_2 \sim 61\,000\,^\circ\mathrm{K}$, as very short-term pure translational pressures and temperatures before the general equilibrium or chemical reaction is established.
The average velocity of the gas molecules in the compression shock is therefore approximately

$$c_{\mathrm{m}\,2} = \sqrt{\frac{3g \cdot \mathscr{R}\,T_2}{M_1}} = 8800\,\mathrm{m\,s^{-1}},$$

i.e. ionization can extend to a noticeable proportion of the total molecules. The majority of all atoms and molecules present could

now participate in the luminescence if the time of passage of the compression shock would be sufficient.
It can also be seen that even higher detonation velocities and lower MACH numbers of the fresh gas –both of which seem to be well within the realm of technical possibility– could result in significantly higher detonation temperatures.
If the planar compression shock considered so far converges as a cylindrical or spherical shock against an axis or a spherical center, then according to GUDERLEY, the pressures increase with the reciprocal distance $r$ from the center of convergence as $r^{-0.396}$ or $r^{-0.792}$ as long as the matter behaves like a normal gas.
At the same time, the velocity $v_1$ of the compression shock approaches infinity with $r \to 0$ and thus also the temperature $T_2$, so that the density of the gas remains finite and does not need to exceed that of the densest possible atomic packing.
These convergent compression shocks form the physical basis of the well-known ballistic hollow charges.
The energy of the total ionization of an atom is known to be approximately $E \sim 2.18 \times 10^{-19} \cdot Z^2$ kJ, where $Z$ is the atomic number; due to the conservation of momentum, the collision energy of thermally agitated particles must be twice as high on average in order to actually trigger the reaction with the energy threshold $E$. The temperature $T_2$ of total ionization is therefore $T_2 \sim 4E/3k_\mathrm{B}$, where $k_\mathrm{B}$ is the BOLTZMANN constant, i.e., $T_2 \sim 2.11 \times 10^5 \cdot Z^2$, and is therefore between $2.11 \times 10^5\,^\circ$K and $1.94 \times 10^9\,^\circ$K for all known atoms.
The corresponding average collision velocities are $v_2 = \sqrt{\frac{4E}{Mm}}$, where $M$ is the atomic mass number and $m = 1.66 \times 10^{-24}$ g is the atomic mass unit. The collision velocity $v_2 = 7.23 \times 10^4 \cdot \sqrt{Z^2/M}$ in $\mathrm{m\,s^{-1}}$ therefore depends on the atomic number and mass number of the atom. In the extreme cases of ${}^{3}_{1}\mathrm{H}$ (with $\sqrt{Z^2/M} = 0.578$) and ${}^{238}_{92}\mathrm{U}$ (with $\sqrt{Z^2/M} = 5.97$), the numerical values are $v_2 = 4.18 \times 10^4\,\mathrm{m\,s^{-1}}$ and $4.32 \times 10^5\,\mathrm{m\,s^{-1}}$, respectively. They are therefore quite close to each other for all conceivable components of the explosive.
This total ionization will play a critical role in the convergent detonation shock insofar as, when the aforementioned temperatures and atomic velocities are exceeded as the shock front approaches the convergence center, only atomic nuclei and electrons will soon remain, i.e., the particle diameters will decrease from $1 \times 10^{-8}$ cm to $1 \times 10^{-12}$ cm and the mean free path lengths of the particles will increase accordingly by about eight orders of magnitude. This will make them significantly larger than the previous thickness of the compression shock of a few atomic free path lengths.
The compression shock will dissipate and a further dynamic in-

crease in temperature will not be possible.
After all, the state of matter described so far is already approaching that found inside normal stars. In particular, the aforementioned limit temperature of $T_2 = 1.94 \times 10^9\,^\circ\mathrm{K}$ for heavy atoms even significantly exceeds the estimated temperatures of the star's interior, which is in the order of about $2 \times 10^7\,^\circ\mathrm{K}$.

# 3. Conclusions from the Theoretical Considerations

This raises the question of whether atomic impact velocities of the order of magnitude $1 \times 10^5\,\mathrm{m\,s^{-1}}$, which are sufficient for the total ionization of atoms and which apparently cannot be significantly exceeded even at the center of a spherical detonation shock, are sufficient to ignite nuclear reactions.
Compared to the velocities of uranium fission fragments of $\sim 1 \times 10^7\,\mathrm{m\,s^{-1}}$, which are considered for similar purposes, this seems unlikely at first glance. The individual ignition temperatures of thermal nuclear reactions can be found approximately from the work $\mathfrak{A}$ in the form

$$\mathfrak{A} = \frac{Z_1 Z_2 \cdot e^2}{(r_1 + r_2)}$$

which is necessary to bring the two nuclei with nuclear charge numbers $Z_1$ and $Z_2$ and nuclear radii $r_1$ and $r_2$ into contact against the Coulomb repulsion

$$\frac{Z_1 Z_2 \cdot e^2}{(r_1 + r_2)^2}$$

of their charges $Z_1 \cdot e$ and $Z_2 \cdot e$ until they come into contact, i.e., to a center-to-center distance of approximately $(r_1 + r_2) \sim 1 \times 10^{-12}\,\mathrm{cm}$. This work is smallest when nuclei with a charge of 1 approach each other and largest when those with a charge of 96 approach each other, and thus lies between $\mathfrak{A}_{1,1} \sim 2.3 \times 10^{-16}\,\mathrm{kJ}$ and $\mathfrak{A}_{96,96} \sim 2.1 \times 10^{-12}\,\mathrm{kJ}$. This means that the ignition temperatures of every possible nuclear collision combination lie between $T = 4\,\mathfrak{A}\,/3k_\mathrm{B} \sim 2.24 \times 10^9\,^\circ\mathrm{K}$ and $2.06 \times 10^{13}\,^\circ\mathrm{K}$, which of course does not mean that every sufficiently energetic collision combination will actually lead to a reaction.
In reaction collisions between particles of different masses, where the loss of momentum of the lighter particle is greater in relation to the heavier particle, the temperature can be up to half as low in the limiting case, i.e., $T = 2\,\mathfrak{A}\,/3k_\mathrm{B}$.
This loss of momentum $\Delta E$ of a particle colliding inelastically at velocity $v$ and mass number $M_1$ with a particle of mass number

$M_2$ assumed to be at rest is given by the classical laws of inelastic collision

$$\frac{\Delta E}{\frac{M_1 \cdot m v^2}{2}} = \frac{1}{1 + \frac{M_1}{M_2}} \,. \tag{24}$$

With $\Delta E = \mathfrak{A}$, this results in

$$v = e \cdot \sqrt{\frac{2 \cdot \left(1 + \frac{M_1}{M_2}\right) \cdot Z_1 Z_2}{(r_1 + r_2) \cdot M_1 m}} \tag{25}$$

as a function of the particle velocity required for the nuclear reaction and the nuclear charge numbers, nuclear mass numbers, and nuclear radii of the collision partners.
The values of required velocities $v$ decrease with $Z/M_1$, i.e., they are smallest when two tritium nuclei ${}^{3}_{1}\mathrm{H}$ collide, namely $v \sim 4.3 \times 10^6\,\mathrm{m\,s^{-1}}$, and increase up to $\sqrt{96 \cdot 3/2} \sim 12$ times when a proton ${}^{1}_{1}\mathrm{H}$ collides with a heavy nucleus of charge 96, i.e., $v \sim 5.1 \times 10^7\,\mathrm{m\,s^{-1}}$. All other collision combinations of different particle types must apparently lie within this relatively narrow velocity range. The particularly favorable, but also particularly rare collision constellation of two tritium nuclei colliding head-on would lead to the even smaller $v = \sqrt{\mathfrak{A}\,/2Mm} \sim 1.5 \times 10^6\,\mathrm{m\,s^{-1}}$.

# 4. Conclusion

If the combustion gas mixture contains very heavy particles alongside very light ones, then according to previous considerations, reactions between these highly dissimilar particles are very unlikely. Their mutual collisions will therefore remain elastic, and according to the classical laws of elastic collision, the light particles will practically absorb the energies of the heavy ones, i.e., the light particles will become more reactive among themselves through the catalytic interaction of the heavy ones. According to these very rough considerations, the very conceivable thermal atomic velocities of $4.32 \times 10^5\,\mathrm{m\,s^{-1}}$ generated by chemical processes are contrasted with the smallest possible nuclear reaction collision velocities of $15 \times 10^5\,\mathrm{m\,s^{-1}}$.
Given the uncertainty of many numerical assumptions, the range appears so small that the fundamental possibility of chemical ignition of thermal nuclear reactions cannot be completely ruled out.

# Part III.
# A vague Calculation regarding Equation 13

In the following I give some hints, how Equation 13 can be transformed into two equations, which are quite simple and exhibit in one case a relation between the (interstellar) number of (charged) particles $N$ and their corresponding number of microstates $\Omega$.
A second rearrangement of Equation 13 establishes a relationship between the natural logarithm of the degree of ionization $\alpha_i$ and $\frac{E}{k_\mathrm{B}T}$ in the form of a straight line equation.
The following auxiliary equations and definitions were used during the transformation of Equation 13:

- The PLANCK units were used as given in `https://de.wikipedia.org/wiki/Planck-Einheiten`.
- The LINDEMANN equation according to [21].
- The equation $\sigma = \frac{1}{n \cdot \lambda}$ for the cross section, where $n = N_A/V$ and $\lambda$ is the mean free path.
- The BEKENSTEIN-HAWKING-entropy according to `https://de.wikipedia.org/wiki/Bekenstein-Hawking-Entropie`, where the surface of the event horizon $A$ was assumed to be $\sigma$.
- The formula for the gravitational constant $G$ according to [24].
- The gas laws, where $V$ is assumed to be a sphere with the radius in the range of the mean free path $\lambda$, so $V = \frac{\pi}{6} \cdot \lambda^3$.
- The frequency of the vibrational mode according to transition state theory of EYRING in the form $\frac{k_\mathrm{B}T}{\hbar}$.
- The gas law $p \cdot V = N \cdot k_\mathrm{B}T$, where $N$ is the number density of the particles and $p$ the pressure.
- In one of the last steps $\frac{E}{k_\mathrm{B}T}$ is substituted with $x$ and integration is performed from 0 to $N$.

Of course, some if not all substitutions or transformations may not be justified in a physical and even more mathematical sense.

As a starting point, Equation 13, the SAHA equation, is written in the form

$$\frac{\alpha_i^2}{\left(1-\alpha_i^2\right)} = \frac{m_\mathrm{el}^{\frac{3}{2}}}{(2\pi)^{\frac{3}{2}} \cdot \hbar^3} \cdot \frac{(k_\mathrm{B}T)^{\frac{5}{2}}}{p} \cdot e^{-\frac{W_0}{k_\mathrm{B}T}} \tag{13}$$

with $\hbar$ being $h/(2\pi)$.

Without giving the details of the calculation the results are as follows:

$$N \simeq \ln\left[(\ln\Omega)^2\right] \tag{I}$$

and

$$\ln\left[\frac{2\alpha_i^2}{(1-\alpha_i^2)}\right] = \frac{E}{k_\mathrm{B}T} + \ln\left[2u - 2\sqrt{2}\cdot ua + ua^2\right], \tag{II}$$

where

$$u \equiv \frac{1}{6\sqrt{2\pi^7}} \cdot \frac{(k_\mathrm{B}T)^{\frac{1}{2}} \cdot \ln(\Omega) \cdot t_\mathrm{P} \cdot \lambda}{\rho^2 \cdot N \cdot (e\cdot\alpha)^2 \cdot l_\mathrm{P}^2 \cdot m_\mathrm{el}^{\frac{1}{2}}}$$
$$a \equiv \frac{\hbar}{l_\mathrm{P} \cdot \rho \cdot m_\mathrm{el}^{\frac{1}{2}} \cdot (k_\mathrm{B}T)^{\frac{1}{2}}} \cdot$$

$N$ is the number of particles (usually atoms or molecules) of the gas or the interstellar medium, $\Omega$ is the number of real microstates (of the black hole) corresponding to the gas's macrostate (or the black hole thermal radiation) as given, e.g., by Boltzmann's entropy formula, $l_\mathrm{P}$ and $t_\mathrm{P}$ are the Planck length and time, respectively, $e$ is Eulers's number, $\alpha$ is the fine-structure constant, $\lambda$ is the mean free path and $\rho$ is the distance or separation of the surfaces of the cross sections of the atoms as a fraction of the distance between two adjacent atomic centers, or, formulated in quantum gravitational terms, the separation of the surfaces of two black holes as a fraction of the distance between two adjacent space-time singularities or their event horizon, respectively.
Equation II may be evaluated, using the ionisation potential instead of the degree of ionisation for $\alpha_i$, as the latter is to my knowledge not tabulated for any element or substance. If this is done with the values of the ionisation potential for the first electron according to [20] and [3] we get Figure 7. The noble gases were not considered, also no exotic elements. In sum 66 elements were considered. For $E$ values for the molar enthalpy of fusion were taken and for $T$ the corresponding melting temperature. The blue regression line in Figure 7 can be approximated with the formula $y(x) = c_0 + c_1 \cdot \ln(x)$ given by

$$\ln\left[\left|\frac{2\alpha_i^2}{(1-\alpha_i^2)}\right|\right] = -0.012625 \cdot \ln\left(\frac{E}{k_\mathrm{B}T}\right) + 1.32132\,. \tag{26}$$

The raw regression parameters obtained are

- $c_0 = 1.321\,32$,
- $c_1 = -0.008\,751\,85$

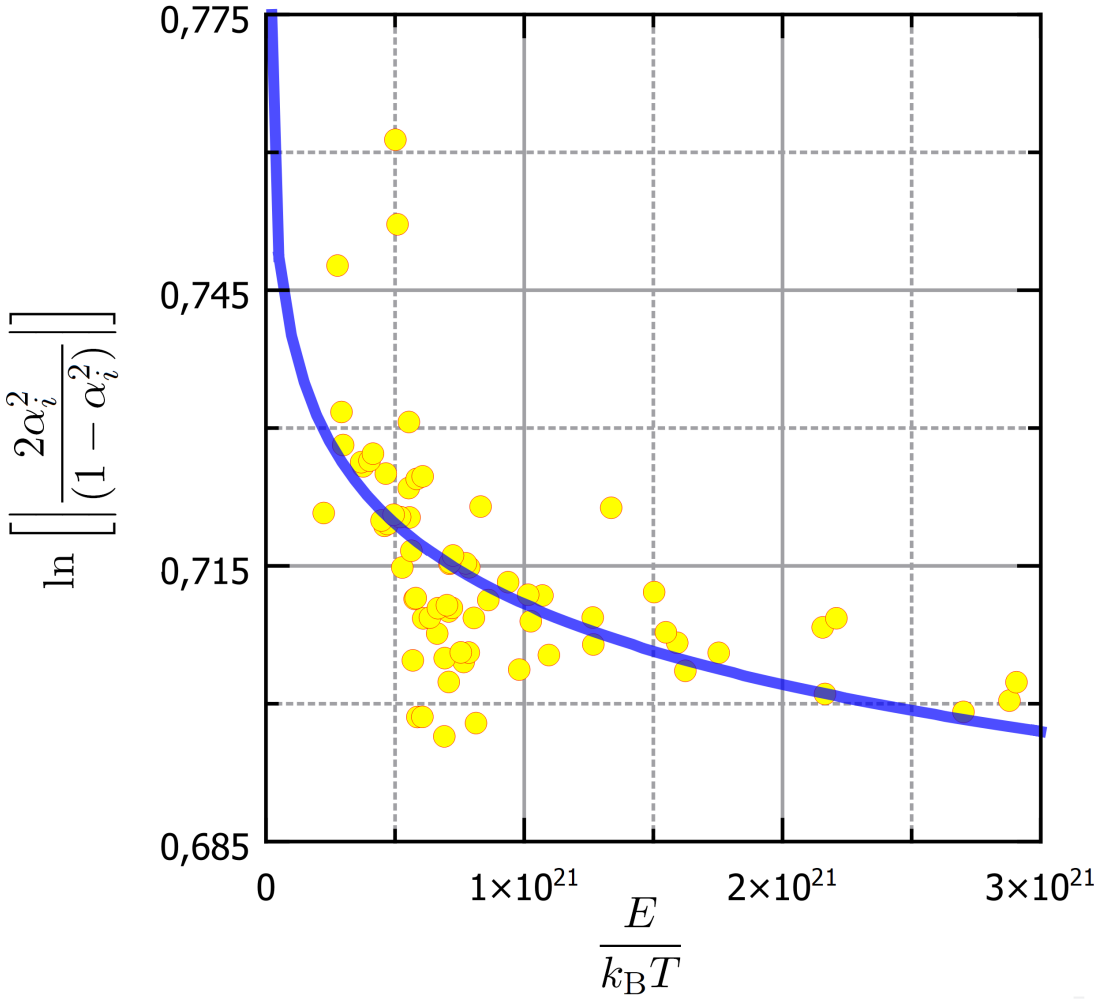


Figure 7: Plot of ionisation potential against molar enthalpy of fusion

with an $R^2 = 0.339$. For $\left(\frac{E}{k_B T}\right) = 0$, i.e., $x = 0$ or zero molar enthalpy of fusion Equation II may therefore be written in the form

$$\ln\left[\frac{2\alpha_i^2}{(1-\alpha_i^2)}\right] \cong 1.321\,, \tag{27}$$

because $-0.00875185 \cdot \ln(x \cong 0) \approx 0$ or a very small number, respectively. Equation 27 is fulfilled for $\alpha_i = 0.631$.
Further, 1.321 equals the last term on the right hand side of Equation II, so we have as a first approximation

$$\begin{aligned} 1.321 &= \ln\left[2u - 2\sqrt{2}\cdot ua + ua^2\right] \\ 1.321 &\approx 1 \\ 1 &\approx \ln\left[2u - 2\sqrt{2}\cdot ua + ua^2\right] \end{aligned}$$

and finally

$$e \approx 2u - 2\sqrt{2}\cdot ua + ua^2\,. \tag{28}$$

# References


[1] I. Bredt. Grundsätzliches über spektroskopische Verfahren zur Messung von Temperaturen und Geschwindigkeiten sehr heißer und sehr schnell strömender Feuergase. *Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für physikalische Chemie*, 56(1):71–84, 1952. https://onlinelibrary.wiley.com/doi/10.1002/bbpc.19520560116.

[2] Ramsauer C. and Kollath R. Über den Wirkungsquerschnitt der Edelgasmoleküle gegenüber Elektronen unterhalb 1 Volt. *Annalen der Physik*, 3:536–564, 1929. https://onlinelibrary.wiley.com/doi/abs/10.1002/andp.19293950405.

[3] F. Cardarelli. *Materials Handbook*. Springer-Verlag London Limited, 2nd edition, 2008.

[4] K. T. Compton and I. Langmuir. Electrical Discharges in Gases. Part I. Survey of Fundamental Processes. *Reviews of Modern Physics*, 2(2):123–242, 1930. https://link.aps.org/doi/10.1103/RevModPhys.2.123.

[5] K. T. Compton and I. Langmuir. Electrical Discharges in Gases Part II. Fundamental Phenomena in Electrical Discharges. *Reviews of Modern Physics*, 3(2):191–257, 1931. https://link.aps.org/doi/10.1103/RevModPhys.3.191.

[6] C. G. Darwin. The refractive index of an ionized medium. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 146(856):17–46, 1934. https://royalsocietypublishing.org/rspa/article/146/856/17-/3662/The-refractive-index-of-an-ionized-medium.

[7] G. Eckart. Sur la propagation des ondes électromagnétiques dans un milieu stratifié 1$^{re}$ partie. *Annals of Telecommunications*, 4(5):142–154, 1949.

[8] G. Eckart. Sur la propagation des ondes électromagnétiques dans un milieu stratifié 2$^{re}$ partie. *Annals of Telecommunications*, 4(6):223–230, 1949.

[9] J. Eggert, Lothar H., and Schwab G.-M. *Lehrbuch der physikalischen Chemie in elementarer Darstellung*. S. Hirzel Verlag, Leipzig, 3rd edition, 1931.

[10] G. J. Elias. Das Verhalten elektromagnetischer Wellen in einen Medium mit räumlich veränderlichen elektrischen Eigenschaften. *Elektrische Nachrichtentechnik*, 8:4–22, 1931.

[11] P. S. Epstein. Reflection of waves in an inhomogeneous absorbing medium. *Proceedings of the National Academy of Sci-*

*ences of the United States of America*, 16(10):627–637, 1930. https://www.pnas.org/doi/epdf/10.1073/pnas.16.10.627.

[12] A. Eucken. *Grundriß der physikalischen Chemie*. Akademische Verlagsgesellschaft Geest & Portig, 6th edition, 1944.

[13] A. Eucken and L. Küchler. StoBanregung intramolekularer Schwingungen. *Physikalische Zeitschrift*, 39:831–835, 1938.

[14] K. Försterling. Über die Ausbreitung des Lichtes in inhomogenen Medien. *Annalen der Physik*, 11(1):1–39, 1931. https://onlinelibrary.wiley.com/doi/10.1002/andp.19314030102.

[15] P. Goerke. Über die Reflexion elektrischer Wellen durch Raketengase. Technical report, Zentralversuchsstelle für Hochfrequenzforschung, Berlin-Gatow et Ulm-Darmstadt, 1944.

[16] G. Guderley. Starke kugelige und zylindrische Verdichtungsstöße in der Nähe des Kugelmittelpunktes bzw. der Zylinderachse. *Zeitschrift für Luftfahrtforschung*, 19:302–312, 1942.

[17] Senftleben H. and Riechemeier O. Der Reaktionsverlauf bei der Bildung von molekularem Wasserstoff aus den Atomen. *Annalen der Physik*, 6:105–128, 1930. https://onlinelibrary.wiley.com/doi/10.1002/andp.19303980106.

[18] H. Haber. Über den Energieaustausch zwischen Translation und Rotation durch Stösse. *Physikalische Zeitschrift*, 17:541–551, 1939.

[19] A. van Itterbeek and P. Mariëns. Measurements with ultrasonics on the velocity and absorption of sound at ordinary and at low temperatures. *Physica*, 4(3):207–215, 1937.

[20] R. D. Lide, editor. *CRC Handbook of Chemistry and Physics*. CRC Press Boca Raton, New York, London, Tokyo, 76th edition, 1995.

[21] F. A. Lindemann. Über die Berechnung molekularer Eigenfrequenzen. *Physikalische Zeitschrift*, 11(14):609–612, 1910. Third last equation for $\nu$ on page 610.

[22] L. B. Loeb. *Fundamental Processes of Electrical Discharges in Gases*. John Wiley & Sons, Inc., 1st edition, 1939. https://archive.org/details/in.ernet.dli.2015.74804.

[23] Royal Society of Chemistry. Collision theory and Maxwell-Boltzmann distribution curves. https://edu.rsc.org/resources/collision-theory-and-maxwell-boltzmann-distribution-curves/4020498.article.

[24] S. Pellis. Exact Mathematical Formula that Connect 6 Dimensionless Physical Constants. *SSRN Electronic Journal*, page 16, 2021. Equation (33) on page 11.

[25] K. Rawer. Elektrische Wellen in einem geschichteten Medium. Zur Frage der partiellen Reflexion und zur Berechnung der scheinbaren Höhe von Ionosphärenschichten. *Annalen der Physik*, 35(5):385–416, 1939. https://onlinelibrary.wiley.com/doi/10.1002/andp.19394270502.

[26] M. N. Saha. LIII. Ionization in the solar chromosphere. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, Series 6*, 40(238):472–488, 1920.

[27] K. Schäfer. Die Stoßanregung intramolekularer Schwingungen in Gasen und Gasmischungen. VII. Theorie der Schalldispersion bei Vorhandensein mehrerer Normalschwingungen. *Zeitschrift für physikalische Chemie*, 46(4):212–228, 1940.

[28] W. Sellmeier. Ueber die durch die Aetherschwingungen erregten Mitschwingungen der Körpertheilchen und deren Rückwirkung auf die ersteren, besonders zur Erklärung der Dispersion und ihrer Anomalien. *Annalen der Physik*, 147(11):386–403, 1872. https://onlinelibrary.wiley.com/doi/abs/10.1002/andp.18722231105.

[29] E. Sänger. Notizen: Hypothese zur Pulververbrennung. *Zeitschrift für Naturforschung A*, 5(8):467–469, 1950.

[30] E. Sänger. Theorie der Gemischaufbereitung in stationären Feuerungen. *Zeitschrift für Brennstoffchemie*, 32(1/2 & 3/4):1–12, 33–55, 1951.

[31] E. Sänger and I. Bredt. Über einen Raketenantrieb für Fernbomber. Technical Report UM 3538, Flugwissenschaftliche Forschungsanstalt München, Ainring (Oberbayern), 1944. https://epizodsspace.airbase.ru/bibl/inostr-yazyki/nemets/Sanger_Bredt.pdf.

[32] E. Sänger, I. Bredt, and P. Goercke. Ionisierung und Lumineszenz in Flammen. *Zeitschrift für angewandte Mathematik und Physik*, 1(3):209–212, 1950. short communication.